PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-053117
(43)Date of publication of application : 27.02.1996

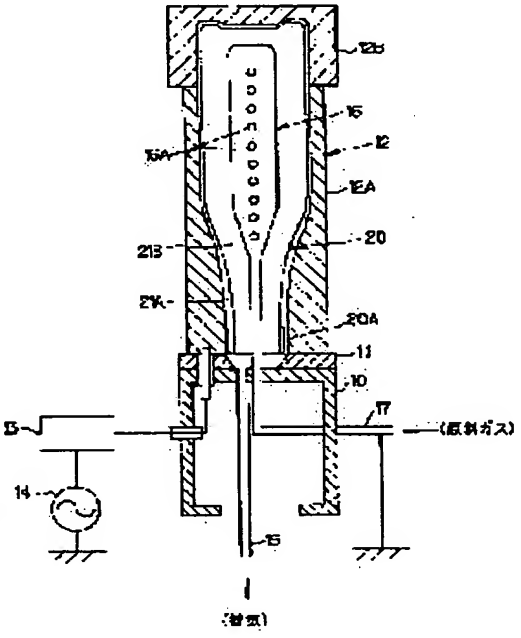
(51)Int.Cl. B65D 1/09

(21)Application number : 06-189224
(22)Date of filing : 11.08.1994

(71)Applicant : KIRIN BREWERY CO LTD
SAMUKO INTERNATL KENKYUSHO:KK
(72)Inventor : NAGASHIMA KAZUFUMI
SHIMA HIDEAKI

(54) METHOD AND DEVICE FOR PRODUCTION OF PLASTIC CONTAINER COATED WITH CARBON FILM

(57)Abstract:
PURPOSE: To prevent sorption of smell with high gas barriering capacity provided by a method wherein hard carbon film is formed by plasma coating to the internal face of a plastic container with an external electrode and an internal electrode similar in figures to the plastic container used.
CONSTITUTION: An external electrode 12 having an internal space 21B approximately similar to and slightly bigger than the external shape of a plastic container 20 is insulated with an insulating plate 11 to which the mouth 20a of the container is brought into contact. An internal electrode 16 to be inserted into the container 20 is approximately similar in shape to the internal wall of the container and has spouts 16A for spouting stock gas while being earthed. After the inside of the external electrode 12 is exhausted with an exhaust pipe 15, stock gas is supplied to the inside of the container 20 through the spouts 16A of the internal electrode 16, and plasma is generated between the external electrode 12 and the internal electrode 16 with high frequency from a high frequency power source 14 applied to the external electrode 12, and thereby hard carbon film is formed uniformly to the internal wall surface of the container 20 placed along the external electrode 12.



LEGAL STATUS

[Date of request for examination]	30.01.1998
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	2788412
[Date of registration]	05.06.1998
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The appearance of the container formed and held in order to hold a container, and the external electrode of the shape of hollow which has the dead air space of an analog mostly, The insulating member which insulates an external electrode while the regio oralis of this container is contacted, when a container is held in the dead air space of this external electrode, The internal electrode inserted from the regio oralis of a container inside the container which was grounded and was held in the dead air space of an external electrode, The manufacturing installation of the carbon film coating plastic envelope characterized by having an exhaust air means for it to be open for free passage in the dead air space of an external electrode, and to perform the exhaust air in dead air space, a supply means to supply material gas inside the container held in the dead air space of an external electrode, and the RF generator connected to the external electrode.
[Claim 2] The configuration of the internal surface of a container where the appearance of said internal electrode is held in the dead air space of an external electrode, and the manufacturing installation of the carbon film coating plastic envelope according to claim 1, with which it is mostly formed in the analog.
[Claim 3] The manufacturing installation of the carbon film coating plastic envelope according to claim 1 with which the material gas which the blow-off hole of material gas is formed in said internal electrode, and is supplied from said supply means blows off from the blow-off hole of an internal electrode in the container held in the dead air space of an external electrode.
[Claim 4] The manufacturing installation of the carbon film coating plastic envelope according to claim 3 with which one or more blow-off holes of said internal electrode are formed.
[Claim 5] The manufacturing installation of the carbon film coating plastic envelope according to claim 1 opened for free passage by the space which a slot is formed in said insulating member, and is formed between the internal surface of an external electrode, and the skin of a container when the regio oralis of the container held by this insulating member in the dead air space of an external electrode is contacted, the interior of a container, and the fang furrow section.
[Claim 6] The manufacturing installation of the carbon film coating plastic envelope according to claim 1 said whose container is a bevel-use bottle.
[Claim 7] The dead air space of an analog is mostly formed in an external electrode with the appearance of the container which holds a container and is held. An external electrode is insulated by the insulating member by which the regio oralis of the container held in this dead air space is contacted. While inserting an internal electrode from the regio oralis of a container inside the container held in dead air space, this internal electrode is grounded. The manufacture approach of the carbon film coating plastic envelope characterized by impressing high frequency to an external electrode after supplying material gas inside the container which exhausted the inside of the dead air space of an external electrode, and was held in the dead air space of an external electrode.

[Claim 8] The manufacture approach of a carbon film coating plastic envelope according to claim 7 that said container is a bevel-use bottle.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates an internal surface to the manufacturing installation and the manufacture approach of a plastic envelope by which coating was carried out with the hard carbon film.
[0002]
[Description of the Prior Art] Generally, the plastic envelope is widely used as a container in the field with the various food fields, drugs fields, etc. from various properties, such as the ease of the shaping, and lightweight nature, a point which is low cost further.
[0003] However, since plastics has the property which penetrates low-molecular gas like oxygen or a carbon dioxide and has the property in which a low-molecular organic compound will sorb the interior further as known well, a plastic envelope receives constraint with the various use gestalten for use compared with other containers, such as glass.
[0004] Here, a sorption means the phenomenon which a low-molecular organic compound permeates, is spread during the presentation of plastics, and is absorbed in plastics. For example, since the drink which is contents will carry out lifting degradation of the oxidization with time, and the carbon dioxide gas of a carbonated drink will penetrate plastics and will be emitted to the exterior of a container by the oxygen which penetrates plastics and permeates the interior of a container when a plastic envelope is filled up with carbonated drinks, such as Biel, a carbonated drink will turn into a drink from which mind escaped.
[0005] Moreover, since the sorption of the aroma components (for example, limonene of orange juice etc.) which are the low-molecular organic compounds contained in a drink is carried out to plastics when a plastic envelope is filled up with the drink which has aroma components, such as orange juice, the presentation of the aroma component of a drink loses balance and there is a possibility that the quality of a drink may deteriorate.
[0006] Moreover, about a plastic envelope, the elution of the low molecular weight compound contained during the presentation may become a problem. That is, when a plastic envelope is filled up with the contents (especially liquid) of which purity is required, the plasticizer contained during the plastics presentation and the additive of a residual monomer and others are eluted in contents, and there is possibility of spoiling purity of contents.
[0007] on the other hand -- recovery of a used container -- current -- although it has social-problem-ized and recycle-ization of a resource is advanced, if it is left before after [use] recovery, and in the environment unlike the case of glassware even if it is going to use a plastic envelope as a re-restoration container, various low-molecular organic compounds, such as a mold odor, will sorb a plastic envelope between them. Since after washing remains in plastics, when using a plastic envelope as a re-restoration container, the low-molecular organic compound by which the sorption was carried out begins to melt gradually into the contents with which it filled up as heterogeneity, and the debasement of contents and a sanitary problem produce this sorbed low-molecular organic compound. For this reason, there is almost no example for which the plastic envelope is used as a returnable container.
[0008] Orientation of the plastics is carried out, in order to control the property in which the property and low-molecular organic compound which penetrate the low-molecular gas of the above plastic envelopes will sorb the interior, crystallinity is raised, or the approach of carrying out the laminating of plastics with more low sorption nature, the thin film of aluminum, etc. is also used, but while all had maintained the special feature of a plastic envelope, the problem of gas barrier nature or a sorption cannot be solved completely.
[0009] Here, the thin film coating technology of the DLC (Diamond Like Carbon) film is known, and what coated laboratory instruments, such as a beaker and a flask, with the DLC film is known conventionally in recent years. This DLC film is SP3 between carbon. It is amorphous carbon which made association the subject, and is the hard carbon film which is very hard, is excellent in insulation, and has very smooth mol FOROJI with a high refractive index.

[0010] Some which were indicated by JP,2-70059,A are one of those used the formation technique of such DLC film for coating of laboratory instrum[illegible] such as a beaker and a flask, conver[illegible]ally.
[0011] The formation equipment of th[illegible]LC film indicated by this JP,2-70059,[illegible] as follows. That is, as shown in drawing 16 , cathode 2 is arranged in the reaction chamber 1 which has inlet 1A and exhaust hole 1B of carbon source gas, and the laboratory instruments 3, such as a beaker, are held in dead-air-space 2A formed in this cathode 2. And after the anode plate 4 grounded inside this laboratory instrument 3 is inserted, the inside of a reaction chamber 1 is decompressed by the exhaust air from exhaust hole 1B. And after carbon source gas is introduced from inlet 1A, a RF is impressed to cathode 3 from RF generator 5, and the DLC film is formed in the front face of a laboratory instrument 3 of the plasma which carbon source gas is excited and is generated.
[0012]
[Problem(s) to be Solved by the Invention] However, the formation equipment of the above-mentioned DLC film Cathode 2 and an anode plate 4 are held in a reaction chamber 1, and it compares with the magnitude of the laboratory instrument 3 whose volume of a reaction chamber 1 is a coating object. Since it is very large, There is much futility of the time amount concerning vacuum actuation and energy, and it has the problem of being difficult further that the formation equipment of this DLC film is a part for 10-1000A/, and a formation rate produces it continuously cheaply since that generation rate is slow.
[0013] Since the formation equipment of this conventional DLC film is aimed at giving added value to this for laboratory instruments, such as a beaker and a flask, a manufacturing cost and production time have seldom been made an issue of, but since what has the cheap restoration container of bevel uses, such as Biel and orange juice, is needed in large quantities, it cannot use this DLC film formation equipment for manufacture of a bevel-use container.
[0014] Moreover, since carbon source gas turns also to the clearance between cathode 2 and the laboratory instrument 3 which is a coating object according to the formation equipment of the above-mentioned DLC film, it cannot limit to the inside of an instrument 3 and coating cannot be performed.
[0015] The restoration container of a bevel use has many opportunities for restoration containers to collide or rub in the selling root again in the production process in works unlike the case of laboratory instruments, such as a beaker and a flask. For this reason, since this DLC film is thin and hard when the DLC film is formed in the external surface of the restoration container of a bevel use, it is possible that the DLC film itself is damaged and the commodity value of a restoration container is spoiled. Therefore, about the restoration container of a bevel use, it is required that the DLC film should be formed only in the internal surface of a container.
[0016] This invention is made in order to solve the above-mentioned conventional trouble. Namely, it is cheap, can produce continuously and aims at offering the manufacturing installation and the manufacture approach of manufacturing the carbon film coating plastic envelope which moreover does not have fear of damage in handling while this invention can solve the problem of the gas barrier nature which plastics has, with the special feature of a plastic envelope maintained, and a sorption, can enable returnable use and can aim at the use range of a plastic envelope, and expansion of a use gestalt.
[0017]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, the manufacturing installation of the carbon film coating plastic envelope by this invention The appearance of the container formed and held in order to hold a container, and the external electrode of the shape of hollow which has the dead air space of an analog mostly, The insulating member which insulates an external electrode while the regio oralis of this container is contacted, when a container is held in the dead air space of this external electrode, The internal electrode inserted from the regio oralis of a container inside the container which was grounded and was held in the dead air space of an external electrode, It is characterized by having an exhaust air means for it to be open for free passage in the dead air space of an external electrode, and to perform the exhaust air in dead air space, a supply means to supply material gas inside the container held in the dead air space of an external electrode, and the RF generator connected to the external electrode. And the manufacturing installation of the carbon film coating plastic envelope by this invention further The appearance of an internal electrode is mostly formed in the analog with the configuration of the internal surface of the container held in the dead air space of an external electrode. The material gas which the blow-off hole of material gas is formed in this internal electrode, and is supplied from a supply means It blows off from the blow-off hole of an internal electrode in the container held in the dead air space of an external electrode. One or more blow-off holes of this internal electrode are formed. Again It is characterized by the space which a slot is formed in an insulating member, and is formed between the internal surface of an external electrode and the skin of a container when the regio oralis of the container held by this insulating member in the dead air space of an external electrode is contacted, the interior of a container, and the fang furrow section being open for free passage.
[0018] In order to attain the above-mentioned purpose, moreover, the manufacture approach of the carbon film

coating plastic envelope by this invention The dead air space of an analog is mostly formed in an external electrode with the appearance of the [redacted]tainer which holds a container and is [redacted]d. An external electrode is insulated by the insulating member by [redacted]hich the regio oralis of the container h[redacted]n this dead air space is contacted. While inserting an internal electrode from the regio oralis of a container inside the container held in dead air space, after supplying material gas inside the container which grounded this internal electrode, exhausted the inside of the dead air space of an external electrode, and was held in the dead air space of an external electrode, it is characterized by impressing a RF to an external electrode.

[0019]

[Function] In an external electrode, a plastic envelope is inserted and the manufacturing installation and the manufacture approach of the above-mentioned carbon film coating plastic envelope are held. At this time, an internal electrode is inserted into a container. And after the regio oralis is contacted by the insulating member and a container is positioned in an external electrode, the inside of an external electrode is sealed. At this time, spacing between the internal surface of an external electrode and the skin of a container is mostly maintained at homogeneity, and spacing between the internal surface of a container and the skin of an internal electrode is also mostly maintained at homogeneity.

[0020] Then, the air in an external electrode is exhausted with an exhaust air means, and the inside of an external electrode is made into a vacuum. At this time, not only the building envelope of a container but the outer space between the skin of a container and the internal surface of an external electrode is exhausted by the slot formed in the insulating member, and it is made a vacuum.

[0021] Then, material gas is supplied from a supply means and it blows off from the blow-off hole formed in the internal electrode to the building envelope of a vacua. Power is supplied to an external electrode from an RF generator after supply of this material gas. By the injection of this power, the plasma is generated between an external electrode and an internal electrode. Although the internal electrode is grounded at this time, since the external electrode is insulated by the insulating member, a negative auto-bias occurs in an external electrode, and a carbon film is formed in the internal surface of the container which met the external electrode by this at homogeneity.

[0022]

[Example] Hereafter, the example of this invention is explained based on a drawing. Drawing 1 shows the manufacturing installation for manufacturing the carbon film coating plastic envelope by this invention. The electric insulating plate 11 made from a ceramic is attached on a pedestal 10, and, as for this manufacturing installation, the external electrode 12 is attached on this electric insulating plate 11. This external electrode 12 serves as the vacuum chamber for DLC film formation, and the space for holding the container 20 for coating in that interior is formed. The space in this external electrode 12 is formed so that it may become large slightly rather than the appearance of the container 20 held there. Although this container 20 is a bevel-use bottle, it may be a container used for other applications.

[0023] The external electrode 12 consists of body section 12A and lid 12B which is attached in the upper part of this body section 12A free [attachment and detachment], and seals the interior of body section 12A. RF generator 14 is connected to this external electrode 12 through the adjustment machine 13. Moreover, the exhaust pipe 15 is opened for free passage by the space in the external electrode 12, and the air in space is exhausted with the vacuum pump which is not illustrated.

[0024] In the space of the external electrode 12, an internal electrode 16 is inserted, and it is arranged so that it may be located in the core of space. This internal electrode 16 is formed so that that appearance can insert from regio-oralis 20A of a container 20 and it may become an analog in the internal configuration of a container 20 mostly. As for spacing of the external electrode 12 and an internal electrode 16, in all locations, it is desirable to make it mostly maintained at homogeneity in 10-150mm.

[0025] The material gas supply pipe 17 is connected to this internal electrode 16, material gas flows into this material gas supply pipe 17 through the quantity-of-gas-flow controller which is not illustrated, and it blows off from blow-off hole 16A formed in the internal electrode 16. When material gas is immediately spread in homogeneity, you may make it form it in one crowning of an internal electrode 16, although it is desirable that more than one are formed in the flank of an internal electrode 16 like illustration as for this blow-off hole 16A in order to make homogeneity diffuse emitted material gas. The internal electrode 16 is grounded through the material gas supply pipe 17.

[0026] So that slot 11A [two or more (this example four pieces)] may be formed and drawing 2 may show, as it expands to drawing 2 and 3 and is shown in an electric insulating plate 11 After the container 20 was held in the external electrode 12 and regio-oralis 20A of a container 20 has been contacted by the electric insulating plate 11, outer space 21A of a container and the exhaust pipe 15 which are formed between the internal surface of the external electrode 12 and the skin of a container 20 are opened for free passage through slot 11A.

[0027] Next, the approach of formation of the DLC film by the above-mentioned manufacturing installation is explained. In the external electrode [redacted]here lid 12B is removed, the containe[redacted] made from plastics is inserted and held from up opening of body section 12A. At this time, an internal electrod[redacted]6 is inserted into a container 20 from regio-oralis 20A of a container 20. And after regio-oralis 20A is contacted on an electric insulating plate 11 and a container 20 is positioned in the external electrode 12, lid 12B is shut and the inside of the external electrode 12 is sealed. At this time, spacing between the internal surface of the external electrode 12 and the skin of a container 20 is mostly maintained at homogeneity, and spacing between the internal surface of a container 20 and the skin of an internal electrode 16 is also mostly maintained at homogeneity.
[0028] Then, the air in the external electrode 12 is exhausted with a vacuum pump, and the inside of the external electrode 12 is made into a vacuum. At this time, not only building envelope 21B of a container 20 but outer space 21A between the skin of a container 20 and the internal surface of the external electrode 12 is exhausted by slot 11A formed in the electric insulating plate 11, and it is made a vacuum. If this does not make outer space 21A a vacuum, either, it is for the inside of this outer space 21A becoming an elevated temperature, and having a bad influence on the plastics quality of the material of a container 20 in the case of plasma generating mentioned later.
[0029] The degree of vacuum at this time has 10-2 - desirable 10-5torr. Supposing ten to one or more degree of vacuums are sufficient as this, when its impurity increases in number too much in a container and it tends to make it less than ten to five degree of vacuum, it is for time amount and energy to start exhausting too much.
[0030] Then, the material gas of a carbon source is supplied to the material gas supply pipe 17 from the quantity-of-gas-flow controller which is not illustrated, and it blows off from blow-off hole 16A formed in the internal electrode 16 in building envelope 21B of a vacua. The amount of supply of this material gas has desirable 1 - 100 ml/min, and the pressure in building envelope 21B is adjusted to less than 0.5-0.001 torrs by supply of this material gas.
[0031] Here, since the inside of outer space 21A is exhausted through slot 11A, the pressure in outer space 21A declines later than the pressure in building envelope 21B for a while. For this reason, as for immediately after exhaust air, the pressure in outer space 21A is high slightly rather than building envelope 21B. Therefore, if material gas is supplied immediately after exhaust air, the material gas which blew off in building envelope 21B will not enter in outer space 21A.
[0032] As material gas, the aliphatic hydrocarbon of a gas or a liquid, aromatic hydrocarbon, oxygenated hydrocarbons, and nitrogen-containing hydrocarbons are used in ordinary temperature. And six or more benzene, toluene, O-xylene, meta xylene, para xylene, a cyclohexane, etc. have an especially desirable carbon number. Although you may use independently, you may make it use these raw materials as two or more sorts of mixed gas. Furthermore, these gas is diluted with rare gas like an argon or helium, and you may make it use it.
[0033] Power is supplied to the external electrode 12 from RF generator 14 through the adjustment machine 13 after supply of this material gas. By the injection of this power, the plasma is generated between the external electrode 12 and an internal electrode 16. Although the internal electrode 16 is grounded at this time, since the external electrode 12 is insulated by the electric insulating plate 11, a negative auto-bias occurs in the external electrode 12, and the DLC film is formed in the internal surface of the container 20 which met the external electrode 12 by this at homogeneity.
[0034] That is, formation of the DLC film in the internal surface of a container 20 is performed by the improved plasma-CVD method. According to this plasma-CVD method, by using the low-temperature plasma, since it can be set as temperature with the comparatively low temperature at the time of formation of the DLC film, when based on bad heat-resistant goods like plastics, it is suitable, and the DLC film of a moreover comparatively cheap and large area can be formed.
[0035] Here, the low-temperature plasma has a high electron temperature in the plasma, when the interior of a reactor is maintained by low voltage, and the temperature of ion or a neutral molecule says the thing of the plasma of a remarkable low condition, i.e., the plasma of the so-called non-equilibrium, compared with it.
[0036] If the plasma occurs between the external electrode 12 and an internal electrode 16, since an electron will be accumulated in the internal surface of the external electrode 12 insulated, the auto-bias of this external electrode 12 is carried out to negative potential. In the external electrode 12 side, about [500-1000V] fall of potential arises for this are recording electron. When it collides with the internal surface of a container 20 located so that the carbon source ionized by plus when the carbon dioxide gas used as a carbon source existed in the plasma at this time may meet the external electrode 12 alternatively and the carbon which subsequently approach joins together, the hard carbon film which becomes the internal surface of a container 20 from the very precise DLC film is formed.
[0037] In addition, the hard carbon film which consists of DLC film is hard carbon film called i carbon film or the hydrogenation amorphous carbon film (a-C:H), and is SP3. It is the thing of the amorphous carbon film which

made association the subject.
[0038] Although it is dependent on the class of the output of high frequency, the pressure of the material gas in a container 20, a distributed gas flow rate, plasma generating time amount, an auto-bias, and raw material etc., as for the thickness of the DLC film, it is desirable to make it set to 0.05-5 micrometers in order to aim at coexistence with the sorption depressor effect of a low-molecular organic compound and the improvement effectiveness of gas barrier nature, adhesion with plastics and endurance, transparency, etc.
[0039] Moreover, the membraneous quality of the DLC film is dependent on the class of the output of high frequency, the pressure of the material gas in a container 20, a distributed gas flow rate, plasma generating time amount, an auto-bias, and raw material etc. similarly. Each of the increment in a high frequency output, pressure reduction of the material gas in a container 20, flow rate reduction of distributed gas, increments in an auto-bias, falls of the carbon number of a raw material, etc. causes hardening of the DLC film, improvement in precision, increase of compressive stress, and increase of brittleness. For this reason, in order to demonstrate the sorption depressor effect and the gas barrier effectiveness of a low-molecular organic compound to the maximum extent, maintaining adhesion with plastics, and membranous endurance, it is desirable that a RF output is set up so that the flow rate of 0.2 - 0.01torr and distributed gas may become [the carbon number of -200--1000V and material gas] 10 - 50 ml/min and an auto-bias may become [the feed gas pressure in 50-1000W, and a container 20] about 1-8 pieces.
[0040] In addition, in order to raise the adhesion of the DLC film and plastics further, plasma treatment is performed and you may make it activate the internal surface of a container 20 by inorganic gas, such as an argon and oxygen, before forming the DLC film.
[0041] Drawing 4 shows the side cross section of the plastic envelope with which the DLC film was formed as mentioned above. 20A shows among drawing the DLC film with which 20B was formed in the internal surface of plastics material 20A in plastics material, respectively. Thus, it not only can decrease remarkably the transmittance of low-molecular inorganic gas like oxygen or a carbon dioxide, but the plastic envelope in which coating was carried out by DLC film 20B in the internal surface can control completely the sorption of various kinds of low-molecular organic compounds which have a smell. Moreover, the transparency which a plastic envelope has is not spoiled by formation of this DLC film.
[0042] in addition, as plastics material which forms a container 20 Polyethylene resin, polypropylene resin, polystyrene resin, cycloolefin copolymer resin, polyethylene terephthalate resin, polyethylenenaphthalate resin, ethylene-vinyl alcohol copolymerization resin, Polly 4-methyl pentene -1 resin, Polymethyl-methacrylate resin, acrylonitrile resin, polyvinyl chloride resin, polyvinylidene chloride resin, styrene-acrylonitrile resin, acrylonitrile-butadien-styrene resin, polyamide resin, polyamidoimide resin, polyacetal resin, Polycarbonate resin, polybutyrene terephthalate resin, ionomer resin, polysulfone resin, polytetrafluoroethylene resin, etc. are mentioned.
[0043] (1) which followed the carbon film coating plastic envelope manufactured by the above-mentioned manufacturing installation and the manufacture approach The thickness of DLC, and (2) The consistency of DLC, and (3) Adhesion 1 and (4) Adhesion 2 and (5) Alkali resistance and (6) Carbon-dioxide-gas barrier nature and (7) Oxygen gas barrier nature and (8) The result of each evaluation of the sorption nature of a low-molecular organic compound (aroma component) is as follows.
[0044] In addition, each evaluation was performed by the following approaches.
(1) the film thickness of DLC -- after masking with the magic marker etc. beforehand at the inside of a container and covering DLC, masking was removed by diethylether etc. and thickness was measured with the product made from Vecco, and the surface type-like measuring instrument DECTACK3.
(2) Measure the weight difference consistency membrane formation before of DLC, and after membrane formation, and it is (1). The consistency was computed from the thickness for which it asked.
(3) About the side-attachment-wall section of adhesion 1 container, it carried out on condition that the following according to the base eye tape method of JISK5400.
[0045] ** clearance spacing [of an incised wound]: -- the number of 1mm** measure eyes : 100 (4) the side-attachment-wall section of adhesion 2 container -- product made from new east science The continuation load type scratch test machine HEIDON 22 was used, and it carried out on condition that the following. Extent of adhesion was expressed with the perpendicular load concerning a scratch needle when the film begins to separate.
[0046]
** The material of a scratch needle, a configuration : a diamond, 50microR** load rate : 100 g/min** table rate : 1000 mm/min (5) The interior of a container was filled up with the alkali solution which added the alkali-proof sodium hydroxide so that it might become 10wt(s)%, it was immersed into the 75-degree C water bath for 24 hours, and the existence of the formation of a form status change of DLC and exfoliation was checked. The

result expressed the thing without change by A and immersion of 12 hours or more by that changeless with immersion of 24 hours or more as go[redacted]
(6) Carbon-dioxide-gas barrier nature MODERN PERMATRANC-4 made from [redacted]NTROL mold was used and the amount of transparency of carbon dioxide gas was measured at 25 degrees C.
(7) Oxygen gas barrier nature MODERN OX-TRANTWIN made from CONTROL was used and the amount of transparency of oxygen was measured at 40 degrees C.
(8) The low-molecular organic compound (aroma component) which has a smell as a kind of the sorption nature environmental material of a low-molecular organic compound (aroma component) was used, and it examined by referring to Matsui's and others approach (J. Agic.Food.Chem., 1992 and 40, 1902-1905).
[0047] The procedure is as follows.
** Make 0.3% sugar ester solution which added 100 ppm (n-octane, n-octanal, n-octanol, ethyl hexanoate, d-limonene) of various aroma components, respectively, and consider as a model flavor solution.
[0048] ** Keep it for one month at 20 degrees C after filling up a container with 700ml of model flavor solutions and covering.
** Discard a model flavor solution one month after, and after 60-degree C distilled water washes the interior of a container, make it dry.
[0049] ** It is filled up with diethylether and extract the aroma component which sorbed the container.
** Take out diethylether from a container, add anhydrous sodium sulfate and dehydrate.
[0050] ** A gas chromatograph performs quantitative analysis by making amyl benzene into an internal standard. A result displays the amount of the aroma component which sorbs a container by mug, when the water solution with which a 1 ppm aroma component exists is in a container. Therefore, a unit serves as mug/ppm/bottle.
[0051] The container made of polyethylene terephthalate resin with a capacity of 700ml (PET made of Mitsui Pet Resin, Type L125) was contained in the external electrode 12 of drawing 1 as a [trial 1] plastic envelope, and it fixed.
[0052] Next, after operating the vacuum pump and making the inside of the external electrode 12 into a vacuum (back pressure) to 10 to 4 or less torrs, as pretreatment, the argon was introduced into the interior of a plastic envelope so that a pressure might serve as 0.04torr(s) by the rate of flow of 30 ml/min, Rf power of 300W was switched on, and plasma treatment of the container inside was carried out. Then, the argon was used for auxiliary gas, toluene, a cyclohexane, benzene, or para xylene was introduced into the interior of a container as material gas, and DLC was covered with the conditions shown in drawing 5 to the inside of a container at homogeneity.
[0053] The result of each evaluation of test-result thickness, a membrane formation rate, a consistency, adhesion 1, adhesion 2, and alkali resistance is as being shown in drawing 6 . Each consistency is 2.00 g/cm3. It had exceeded and the film was very precise.
[0054] As a result of the base eye trial, the adhesion with polyethylene terephthalate resin was good, and it became clear that it can be equal to actual use enough. Moreover, the alkali resistance of the film of DLC was extremely stable satisfactory, and it became clear that polyethylene terephthalate resin was protected completely.
[0055] About oxygen transmittance, carbon-dioxide transmittance, and extent of the sorption of various aroma components, the result is shown in drawing 7 . The film of precise DLC not only controls the sorption of an aroma component completely, but controlled transparency of oxygen and a carbon dioxide effectively.
[0056] Moreover, the transparency spectrum in the ultraviolet visible region of the drum section of the plastic envelope which covered DLC inside is shown in drawing 8 . It applied to the ultraviolet region from about 500nm order, transmission was decreasing rapidly, and it was suggested that coating of the DLC film is effective in controlling degradation by the ultraviolet rays of contents.
[0057] Drawing 9 is the Raman spectrum of the thin film covered with the conditions of trial 1 by the drum section of a plastic envelope.
Except that the container made of polyacrylonitrile styrene copolymer resin with a capacity of 700ml (Monsanto, Mitsubishi, formation make-AN resin, Type L700) was used as a [trial 2] plastic envelope, the DLC film was formed in the container inside by the same approach as trial 1. The conditions of formation of the DLC film are as being shown in drawing 10 . Moreover, each trial was performed like the trial 1 about thickness, a consistency, adhesion 1, adhesion 2, alkali resistance, carbon-dioxide-gas barrier nature, oxygen gas barrier nature, and the sorption nature of a low-molecular organic compound.
[0058] The test result about test-result thickness, a film formation rate, a consistency, adhesion 1, adhesion 2, and alkali resistance is as being shown in drawing 11 . About thickness and a consistency, it was good like the case of trial 1. Moreover, about adhesion 1 and adhesion 2, it became clear that it is satisfactory like the case of trial 1, and the adhesion of DLC and acrylonitrile styrene copolymer resin was the same as that of polyethylene

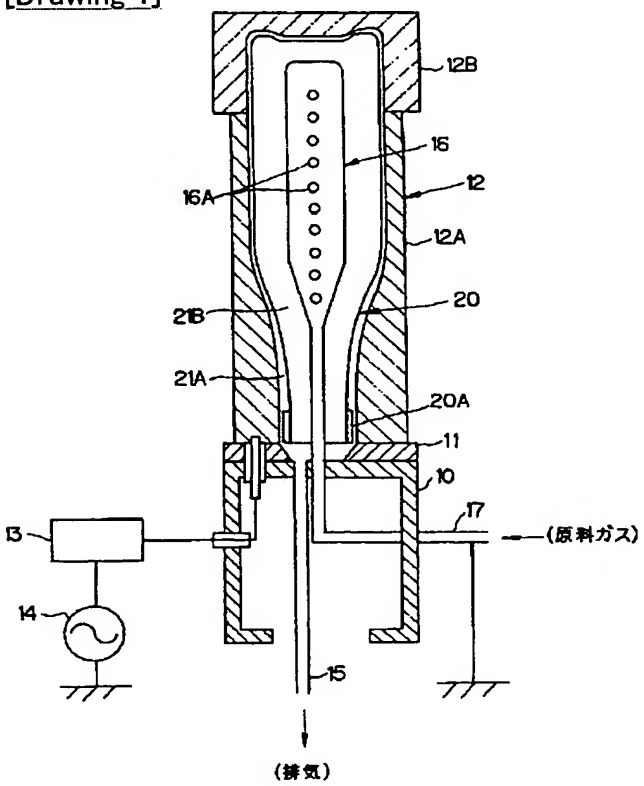
terephthalate resin, and it was satisfactory practically.
[0059] About oxygen transmittance, carbon-dioxide transmittance, and extent of the sorption of various aroma components, the result is shown in drawing 12 . That is, originally acrylonitrile styrene copolymer resin is excellent in gas barrier nature, and is having covered DLC further, and it became clear that the amount of transparency of oxygen and a carbon dioxide reaches very low level. Like the trial 1, the amount of sorptions of various aroma components was below limit of detection, and was satisfactory also in organic-functions evaluation.
[0060] DLC was covered with the same approach as trial 1 inside the container except having used the container made of cycloolefin copolymer resin with a capacity of 700ml (the product made from the Mitsui petrochemistry: COC resin type APL 6015) as a [trial 3] plastic envelope. The conditions of formation of the DLC film are shown in drawing 13 . Moreover, each trial of thickness, a consistency, adhesion 1, adhesion 2, alkali resistance, carbon-dioxide-gas barrier nature, oxygen gas barrier nature, and the sorption nature of a low-molecular organic compound as well as trial 1 was performed.
[0061] The result of each trial of test-result thickness, a membrane formation rate, a consistency, adhesion 1, adhesion 2, and alkali resistance is shown in drawing 14 . Like the trial 1 and the trial 2, it was satisfactory also about which trial item, and especially the adhesion of a plastic envelope and DLC was very good.
[0062] About the sorption nature of oxygen transmittance, carbon-dioxide transmittance, and various aroma components, the result is shown in drawing 15 . Although oxygen transmittance, carbon-dioxide transmittance, and its amount of aroma component sorptions were comparatively large since cycloolefin copolymer resin was olefin system resin, it became clear by covering with DLC that it could control to remarkable level.
[0063]
[Effect of the Invention] As mentioned above, according to the manufacturing installation and the manufacture approach of a carbon film coating plastic envelope by this invention, in order that the futility of energy may not have production time short, either, it becomes possible to produce continuously a cheap carbon film coating plastic envelope. Furthermore, a carbon film can be limited and formed only in the internal surface of a container.

[0064] By forming an internal electrode in an analog mostly with the configuration of the internal surface of a container, a carbon film can be formed in the internal surface of a container at homogeneity. By forming the blow-off hole of material gas in an internal electrode, material gas blows off from the core of a container to homogeneity, and diffusion of material gas is further promoted by forming one or more these blow-off holes.
[0065] Furthermore, space between the internal surface of an external electrode and the skin of a container is also made a vacuum by the slot formed in an insulating member, and the temperature rise at the time of plasma generating can be suppressed by this. Moreover, when the container manufactured by this invention is a bevel-use bottle, it can be used as a returnable container instead of the conventional glassware.

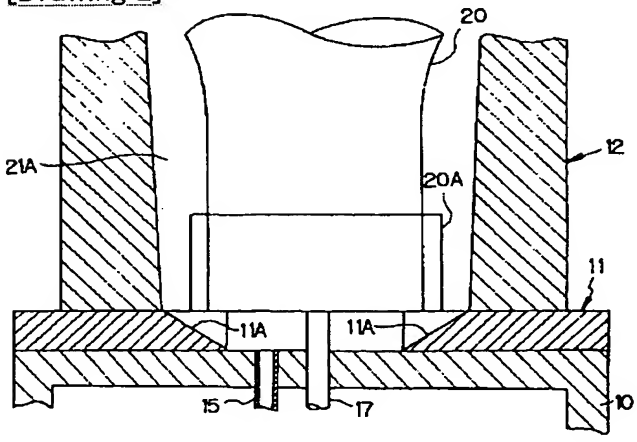
[Translation done.]

DRAWINGS

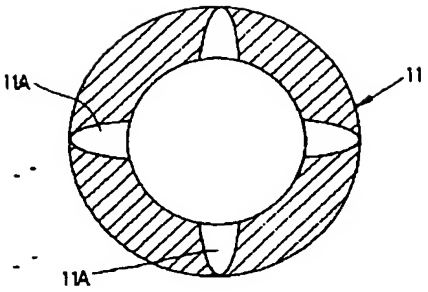
[Drawing 1]



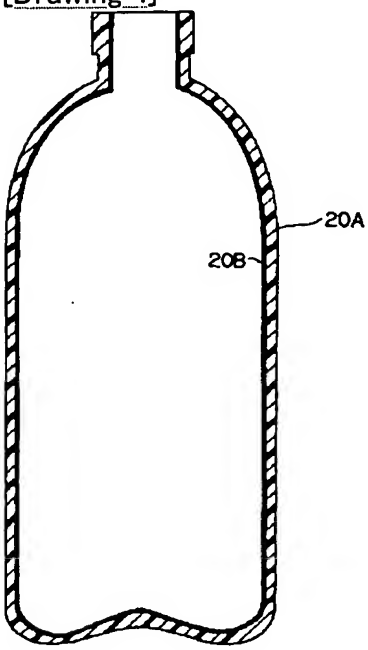
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Drawing 5]

実験NO.	原料		補助ガス			出力	自己バイアス	時間
	種類	圧力	種類	流量	圧力			
		(Torr)		(ml/min)	(Torr)	(W)	(V)	(S)
1	n-ヘキサン	0.04	なし	—	—	400	-680	10
2	n-ヘキサン	0.10	なし	—	—	400	-571	10
3	n-ヘキサン	0.04	アルゴン	30	0.04	400	-678	10
4	n-ヘキサン	0.04	なし	—	—	500	-731	10
5	n-ヘキサン	0.04	なし	—	—	200	-466	10
6	n-ヘキサン	0.02	なし	—	—	400	-740	10
7	シクロヘキサン	0.04	なし	—	—	400	-714	10
8	ベンゼン	0.04	なし	—	—	400	-700	10
9	P-キシレン	0.04	なし	—	—	400	-666	10
10	n-ヘキサン	0.04	なし	—	—	400	-683	20
11	n-ヘキサン	0.02	アルゴン	30	0.02	500	-725	10
12	n-ヘキサン	0.02	アルゴン	40	0.04	500	-706	10

[Drawing 6]

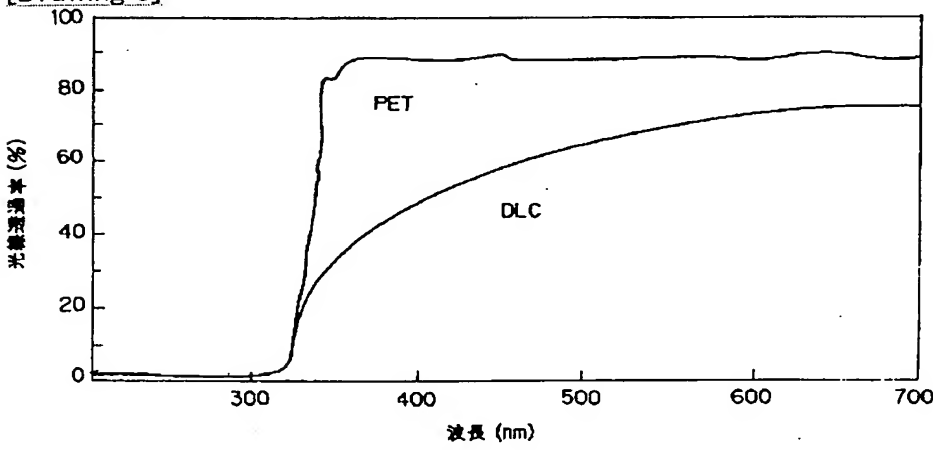
実験 NO.	膜厚 (Å)	密度 (g/cm³)	密着性 1	密着性 2(g)	耐アルカリ性
1	1878	2.23	[redacted]	19.4	◎
2	2756	1.88	100/100	21.7	◎
3	1644	2.54	100/100	19.4	◎
4	2207	2.84	100/100	21.8	◎
5	1531	1.61	100/100	17.7	◎
6	1069	2.75	100/100	19.9	◎
7	1702	2.31	100/100	16.6	◎
8	1761	2.42	100/100	17.0	◎
9	1993	2.11	100/100	19.5	◎
10	4174	2.28	100/100	26.1	◎
11	1001	2.64	100/100	17.7	◎
12	922	2.82	100/100	18.1	◎

注1：密着性 1　：100の桝目に対し、剥離しなかった桝目の数
注2：耐アルカリ性：◎ 優　○ 良　× 剥離

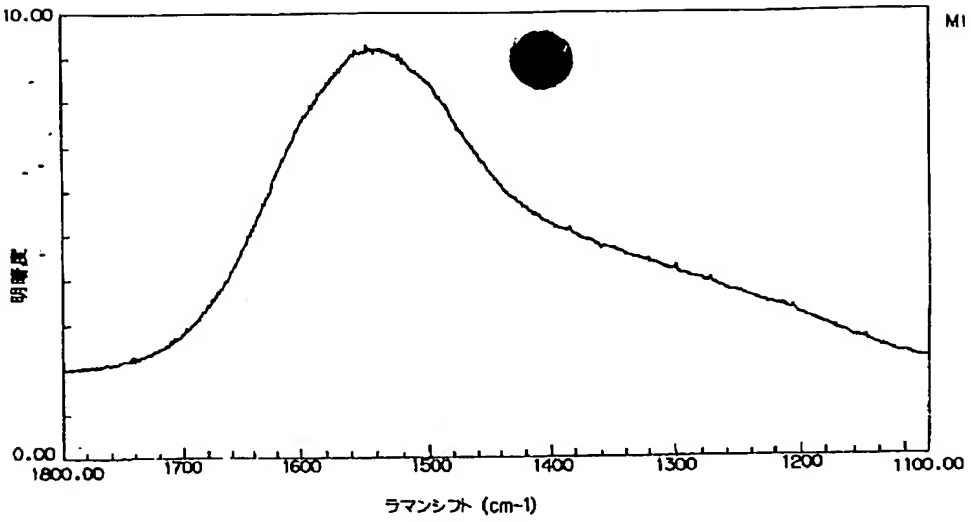
[Drawing 7]

実験 NO.	酸素透過度	二酸化炭素透過度	収着 (μg/ppm/bottle)				
	(μl/day/pkg)	(μl/day/pkg)	オクタン	オクタナール	オクタノール	ヘキサン酸エチル	d-リモネン
未処理PETボトル	43.7	142.4	21.98	81.31	37.38	40.18	56.32
1	7.8	14.8	—	—	—	—	—
2	6.2	12.2	—	—	—	—	—
3	7.5	14.4	—	—	—	—	—
4	4.3	11.9	—	—	—	—	—
5	8.9	15.7	—	—	—	—	—
6	5.6	13.6	—	—	—	—	—
7	5.6	13.0	—	—	—	—	—
8	5.5	12.5	—	—	—	—	—
9	5.4	12.6	—	—	—	—	—
10	5.0	11.9	—	—	—	—	—
11	5.7	14.3	—	—	—	—	—
12	6.0	14.0	—	—	—	—	—

[Drawing 8]



[Drawing 9]



[Drawing 10]

実験NO.	原料		補助ガス			出力	自己バイアス	時間
	種類	圧力 (Torr)	種類	流量 (ml/min)	圧力 (Torr)	(W)	(V)	(S)
1	n-ヘキサン	0.04	なし	—	—	400	-688	10
2	n-ヘキサン	0.10	なし	—	—	400	-556	10
3	n-ヘキサン	0.04	アルゴン	30	0.04	400	-670	10
4	n-ヘキサン	0.04	なし	—	—	500	-725	10
5	n-ヘキサン	0.04	なし	—	—	200	-459	10
6	n-ヘキサン	0.02	なし	—	—	400	-733	10
7	シクロヘキサン	0.04	なし	—	—	400	-713	10
8	ベンゼン	0.04	なし	—	—	400	-695	10
9	P-キシレン	0.04	なし	—	—	400	-657	10
10	n-ヘキサン	0.04	なし	—	—	400	-683	20
11	n-ヘキサン	0.02	アルゴン	30	0.02	500	-716	10
12	n-ヘキサン	0.02	アルゴン	40	0.04	500	-700	10

[Drawing 11]

実験 NO.	膜厚 (Å)	密度 (g/cm³)	密着性 1	密着性2(g)	耐アルカリ性
1	1962	2.11	100/100	25.8	◎
2	2711	1.97	100/100	23.3	◎
3	1698	2.62	100/100	20.6	◎
4	2315	2.73	100/100	29.5	◎
5	1457	1.54	100/100	26.6	◎
6	1112	2.66	100/100	27.7	◎
7	1776	2.21	100/100	19.3	◎
8	1809	2.65	100/100	22.5	◎
9	2076	2.23	100/100	24.4	◎
10	4003	2.19	100/100	31.9	◎
11	954	2.88	100/100	22.1	◎
12	1011	2.94	100/100	24.1	◎

注1：密着性 1　：100の桝目に対し、剥離しなかった桝目の数
注2：耐アルカリ性：◎ 優　○ 良　× 剥離

[Drawing 12]

実験 NO.	酸素透過度	二酸化炭素透過度	吸着				
	(μl/day/pkg)	(μl/day/pkg)	オクタン	[redacted]タナール	オクタノール	ヘキサン酸エチル	d-リモネン
未処理PANボトル	33.8	119.8	3.64	4.01	9.55	6.16	10.32
1	2.2	7.8	—	—	—	—	—
2	1.9	6.5	—	—	—	—	—
3	2.5	6.7	—	—	—	—	—
4	1.4	3.2	—	—	—	—	—
5	2.2	9.6	—	—	—	—	—
6	2.0	5.3	—	—	—	—	—
7	1.9	6.1	—	—	—	—	—
8	1.7	6.0	—	—	—	—	—
9	1.6	5.4	—	—	—	—	—
10	1.0	5.2	—	—	—	—	—
11	1.3	7.1	—	—	—	—	—
12	1.6	7.3	—	—	—	—	—

[Drawing 13]

実験NO.	原料		補助ガス			出力	自己バイアス	時間
	種類	圧力	種類	流量	圧力			
		(Torr)		(ml/min)	(Torr)	(W)	(V)	(S)
1	n-ヘキサン	0.04	なし	—	—	400	-677	10
2	n-ヘキサン	0.10	なし	—	—	400	-571	10
3	n-ヘキサン	0.04	アルゴン	30	0.04	400	-692	10
4	n-ヘキサン	0.04	なし	—	—	500	-755	10
5	n-ヘキサン	0.04	なし	—	—	200	-476	10
6	n-ヘキサン	0.02	なし	—	—	400	-721	10
7	シクロヘキサン	0.04	なし	—	—	400	-719	10
8	ベンゼン	0.04	なし	—	—	400	-696	10
9	P-キシレン	0.04	なし	—	—	400	-670	10
10	n-ヘキサン	0.04	なし	—	—	400	-691	20
11	n-ヘキサン	0.02	アルゴン	30	0.02	500	-728	10
12	n-ヘキサン	0.02	アルゴン	40	0.04	500	-700	10

[Drawing 14]

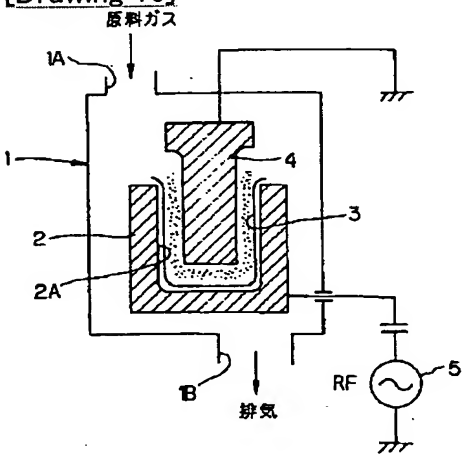
実験 NO.	膜厚 (Å)	密度 (g/cm^3)	密着性 1	密着性2(g)	耐アルカリ性
1	1978	2.33	100/100	26.5	◎
2	3005	1.95	100/100	27.2	◎
3	1891	2.61	100/100	26.4	◎
4	2564	2.81	100/100	27.5	◎
5	1611	1.72	100/100	24.3	◎
6	1322	2.77	100/100	22.1	◎
7	1883	2.29	100/100	20.0	◎
8	1926	2.44	100/100	23.3	◎
9	2079	2.08	100/100	28.9	◎
10	4537	2.35	100/100	31.1	◎
11	1147	2.71	100/100	22.5	◎
12	1005	2.81	100/100	25.2	◎

注1：密着性 1　：100の桝目に対し、剥離しなかった桝目の数
注2: 耐アルカリ性：◎ 優　○ 良　× 剥離

[Drawing 15]

実験 NO.	酸素透過度	二酸化炭素透過度	収着 (μg/ppm/bottle)				
	(μl/day/pkg)	(μl/day/pkg)	オクタン	[redacted]ール	オクタノール	ヘキサン酸エチル	d-リモネン
未処理COCボトル	362.5	566.9	121.54	95.82	33.61	62.59	181.91
1	39.7	60.8	—	—	—	—	—
2	31.1	51.9	—	—	—	—	—
3	42.5	57.7	—	—	—	—	—
4	22.3	42.3	—	—	—	—	—
5	46.8	66.7	—	—	—	—	—
6	33.3	60.0	—	—	—	—	—
7	31.8	56.4	—	—	—	—	—
8	29.5	50.1	—	—	—	—	—
9	28.4	43.9	—	—	—	—	—
10	26.6	42.2	—	—	—	—	—
11	30.0	52.5	—	—	—	—	—
12	30.7	54.6	—	—	—	—	—

[Drawing 16]



[Translation done.]

CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
[Section partition] The 6th partition of the 2nd section
[Publication date] May 25, Heisei 11 (1999)

[Publication No.] Publication number 8-53117
[Date of Publication] February 27, Heisei 8 (1996)
[Annual volume number] Open patent official report 8-532
[Application number] Japanese Patent Application No. 6-189224
[International Patent Classification (6th Edition)]

B65D 1/09

[FI]

B65D 1/00 B

[Procedure revision]
[Filing Date] January 30, Heisei 10
[Procedure amendment 1]
[Document to be Amended] Specification
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[Proposed Amendment]
[Claim(s)]
[Claim 1] The appearance of the container with which the wall section of dead air space is held while it has the dead air space in which a container is held and this dead air space forms a vacuum chamber, and the external electrode of the shape of hollow mostly formed in the analog,
The insulating member which insulates an external electrode while the regio oralis of this container is contacted, when a container is held in the dead air space of this external electrode,
The internal electrode inserted from the regio oralis of a container inside the container which was grounded and was held in the dead air space of an external electrode,
An exhaust air means for it to be open for free passage in the dead air space of an external electrode, and to perform the exhaust air in dead air space,
A supply means to supply material gas inside the container held in the dead air space of an external electrode,
The manufacturing installation of the carbon film coating plastic envelope characterized by having the RF generator connected to the external electrode.
[Claim 2] The configuration of the internal surface of a container where the appearance of said internal electrode is held in the dead air space of an external electrode, and the manufacturing installation of the carbon film coating plastic envelope according to claim 1, with which it is mostly formed in the analog.
[Claim 3] The manufacturing installation of the carbon film coating plastic envelope according to claim 1 with which the material gas which the blow-off hole of material gas is formed in said internal electrode, and is supplied from said supply means blows off from the blow-off hole of an internal electrode in the container held in the dead air space of an external electrode.
[Claim 4] The manufacturing installation of the carbon film coating plastic envelope according to claim 3 with which one or more blow-off holes of said internal electrode are formed.
[Claim 5] The manufacturing installation of the carbon film coating plastic envelope according to claim 1 opened

for free passage by the space which a slot is formed in said insulating member, and is formed between the internal surface of an external electro[redacted]and the skin of a container when the [redacted]o oralis of the container held by this insulating member in the dead [redacted]space of an external electrode is cont[redacted]ed, the interior of a container, and the fang furrow section.
[Claim 6] The manufacturing installation of the carbon film coating plastic envelope according to claim 1 said whose container is a bevel-use bottle.
[Claim 7] The dead air space of an analog is mostly formed in an external electrode with the appearance of the container which holds a container and is held. An external electrode is insulated by the insulating member by which the regio oralis of the container held in this dead air space is contacted. While inserting an internal electrode from the regio oralis of a container inside the container held in dead air space, this internal electrode is grounded. The manufacture approach of the carbon film coating plastic envelope which exhausts the inside of the dead air space of an external electrode, makes a vacuum the inside of this dead air space, and is characterized by impressing high frequency to an external electrode after supplying material gas inside the container held in the dead air space of an external electrode.
[Claim 8] The manufacture approach of a carbon film coating plastic envelope according to claim 7 that said container is a bevel-use bottle.
[Claim 9] The manufacture approach of the carbon film coating plastic envelope according to claim 7 which maintains mostly at homogeneity spacing between the internal surface of said external electrode, and the skin of the container held in this external electrode, and spacing between the internal surface of this container, and the skin of an internal electrode.
[Claim 10] The manufacture approach of the carbon film coating plastic envelope according to claim 7 which forms a slot in said insulating member and also exhausts the outer space between the skin of a container, and the internal surface of an external electrode with the building envelope of a container through this slot.
[Claim 11] The manufacture approach of the carbon film coating plastic envelope according to claim 10 which supplies material gas inside the container held in the dead air space of an external electrode immediately after exhaust air of the outer space between the skin of said container, and the internal surface of an external electrode.
[Claim 12] The manufacture approach of a carbon film coating plastic envelope according to claim 7 that inorganic gas performs plasma treatment before carrying out carbon film coating at a plastic envelope.
[Claim 13] The manufacture approach of a carbon film coating plastic envelope according to claim 7 that the degree of vacuums by the exhaust air in the dead air space of an external electrode are 10-2 - 10-5torr.
[Procedure amendment 2]
[Document to be Amended] Specification
[Item(s) to be Amended] 0017
[Method of Amendment] Modification
[Proposed Amendment]
[0017]
[Means for Solving the Problem] This invention is characterized by providing the following in the manufacturing installation of a carbon film coating plastic envelope, in order to attain the above-mentioned purpose. The external electrode of the shape of the appearance of the container with which the wall section of dead air space is held while it has the dead air space in which a container is held and this dead air space forms a vacuum chamber, and hollow mostly formed in the analog The insulating member which insulates an external electrode while the regio oralis of this container is contacted, when a container is held in the dead air space of this external electrode The internal electrode inserted from the regio oralis of a container inside the container which was grounded and was held in the dead air space of an external electrode An exhaust air means for it to be open for free passage in the dead air space of an external electrode, and to perform the exhaust air in dead air space, a supply means to supply material gas inside the container held in the dead air space of an external electrode, and the RF generator connected to the external electrode And the manufacturing installation of the carbon film coating plastic envelope by this invention further The appearance of an internal electrode is mostly formed in the analog with the configuration of the internal surface of the container held in the dead air space of an external electrode. The material gas which the blow-off hole of material gas is formed in this internal electrode, and is supplied from a supply means It blows off from the blow-off hole of an internal electrode in the container held in the dead air space of an external electrode. One or more blow-off holes of this internal electrode are formed. Again It is characterized by the space which a slot is formed in an insulating member, and is formed between the internal surface of an external electrode and the skin of a container when the regio oralis of the container held by this insulating member in the dead air space of an external electrode is contacted, the interior of a container, and the fang furrow section being open for free passage.
[Procedure amendment 3]

[Document to be Amended] Specification
[Item(s) to be Amended] 0018
[Method of Amendment] Modification
[Proposed Amendment]
[0018] In order to attain the above-mentioned purpose, moreover, the manufacture approach of the carbon film coating plastic envelope by this invention The dead air space of an analog is mostly formed in an external electrode with the appearance of the container which holds a container and is held. An external electrode is insulated by the insulating member by which the regio oralis of the container held in this dead air space is contacted. While inserting an internal electrode from the regio oralis of a container inside the container held in dead air space, this internal electrode is grounded. The inside of the dead air space of an external electrode is exhausted, and the inside of this dead air space is made into a vacuum, and after supplying material gas inside the container held in the dead air space of an external electrode, it is characterized by impressing a RF to an external electrode.

[Translation done.]